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Self-Assembled Monolayers

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Biological and Biomimetic Materials - Properties to Function

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Helical, Disordered, and What that Means: Structural Characterization of a New Series of Methyl 1-Thiaoligo(ethylene Oxide) Self-Assembled Monolayers

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ABSTRACT

Self-assembled monolayers (SAMs) of a series of linear thiols containing a 1-thiaoligo(ethylene oxide) [TOEO] moiety, i.e., $\text{HS}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$, where $x = 3 - 6$, were prepared on polycrystalline gold (Au) and characterized by reflection absorption infrared spectroscopy (RAIRS) and spectroscopic ellipsometry (SE). For $x = 5$ and 6, the RAIRS data show that the TOEO segment, oriented normal to the substrate, adopts the highly ordered 7/2 helical structure of the folded-chain crystal polymorph of poly(ethylene oxide). For $x = 3$ and 4, the RAIRS and SE data indicate disordered, "amorphous" SAMs with essentially no evidence of the helical conformation in the TOEO segment. These data suggest that, for SAMs with TOEO segments, a minimum of five ethylene oxide units is required to adopt a helical conformation.

INTRODUCTION

Biocompatible materials for biomedical devices and diagnostic technologies continue to be an area of intense interest.¹ A central issue for much of this activity is surfaces that are resistant to the adsorption of proteins.² Protein resistant surfaces are desirable for implants (prostheses, pacemaker electrodes³, etc.), contact lenses⁴ and inert matrices for chemical and biosensors.⁵ Self-assembled monolayers (SAMs) of ω -oligo(ethylene oxide) [ω -OEO] alkylthiols or alkylsilanes, where $\text{OEO} = (\text{CH}_2\text{CH}_2\text{O})_x$, $x = 3 - 6$, ~ 17 , or ~ 144 , and $R = \text{H}$ or CH_3 , assembled on Au ⁶⁻¹¹ or SiO_2 ^{12,13}, respectively, have been found to be highly protein resistant. For the SAMs on Au with short OEO segments ($x = 3$ or 6), protein resistance was attributed to a film of water on helical OEO conformations.⁷ However, RAIRS data for these SAMs, is most consistent with the OEO segments as mixtures of helical and non-helical conformations.

In contrast to the above ω -OEO SAMs of mixed conformations, essentially all helical, near single phase OEO segments have been reported for the SAMs of $\text{HS}(\text{CH}_2\text{CH}_2\text{O})_6\text{R}$, where $R = \text{CH}_3$, $\text{C}_{10}\text{H}_{21}$ and $\text{C}_{18}\text{H}_{37}$.^{14,15} The RAIRS spectra of these alkylated 1-thiahexa(ethylene oxide) [THEO] SAMs, which position the OEO segments closer to the Au, nearly exactly match the spectral characteristics of the 7/2 helix of the folded-chain crystal polymorph of crystalline poly(ethylene oxide).¹⁶ In addition, the RAIRS spectra of these SAMs do not show bands at $\sim 1130\text{ cm}^{-1}$ and $\sim 1145\text{ cm}^{-1}$ indicative of OEO segments in amorphous¹⁷ and/or all-*trans* conformations⁷, respectively. The THEO segments in these SAMs likely adopt the highly ordered, helical conformation because of a nearly perfect match between the cross-sectional area of the helix, 21.38 \AA^2 , and the packing density, $21.4\text{ \AA}^2/\text{thiolate}$ ¹⁸, of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer on Au [assuming predominantly (1 1 1) Au with $\text{S} - \text{S} \equiv 0.50\text{ nm}$].

This paper compares the structures for the SAMs of $\text{HS}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$, where $x = 3 - 6$. Our interest in this homologous series is based on two very different ideas. On the one hand, SAMs with $x < 6$ that have the TOEO segments identical with $x = 6$ (ordered, helical) would be potential standard ultrathin films in the 1 - 2 nm range. As discussed previously, SAMs of increasing OEO length that have the OEO segments in the 7/2 helix would be isostructural and film thickness would increase in a predictable manner.^{19,20} Alternatively, if the SAMs with $x < 6$ do not have helical TOEO segments, then these surfaces would be candidates for protein resistant surfaces because ordered, helical SAMs were found not to be protein resistant.¹⁴

EXPERIMENTAL DETAILS²¹

Synthesis. The compounds $\text{HS}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$ [hereafter referred to as $(\text{EO})_x\text{CH}_3$], where $x = 3 - 6$, were prepared by conversion of the corresponding oligo(ethylene oxide) monomethyl ether (TCI America, Inc., Portland, OR) to the bromide [trifluoroacetic anhydride/tetrahydrofuran (THF)] followed by reaction with LiBr/THF-[hexamethylphosphoramide (HMPA)]. The thiols were then prepared by first converting the bromides to the thiol acetates ($\text{CH}_3\text{COSNa/MeOH}$), followed by hydrolysis ($\text{H}_3\text{O}^+/\text{MeOH}$). Structural assignments were made from proton nuclear magnetic resonance and high resolution mass spectrometry data.²² Sample purity (>98%) was determined from thin-layer chromatography (TLC) analysis (one spot by TLC). All chemicals, except THF, were purchased from Aldrich Chemical Co., (Milwaukee, WI). THF (Mallinckrodt AR) was purchased from North Strong Scientific (Phillipsburg, NJ). THF and HMPA were distilled from calcium hydride. The THF was distilled under N_2 immediately before use; whereas the HMPA was distilled and stored under N_2 over 0.3 nm molecular sieves.

Sample Preparation. Silicon (1 0 0) wafers (Virginia Semiconductor, Fredricksburg, VA) were initially coated with chromium (~2 nm) and then with gold (~200 nm) by magnetron sputtering (Edwards Auto 306, UK) at a base pressure of $\sim 1.3 \times 10^{-6}$ mbar as described previously.¹⁵ The monolayers were prepared by immediately immersing the gold substrates in $\sim 0.5 \times 10^{-3}$ mol/L solutions of the corresponding thiol in distilled 95% ethanol for at least 18 h, unless otherwise stated.

Visible Spectroscopic Ellipsometry (SE). Multiple wavelength ellipsometric measurements were performed on a J. A. Woollam Co., Inc. (Lincoln, NE) M-44 spectroscopic ellipsometer aligned at a nominal incidence angle of $\sim 70^\circ$ as described elsewhere.²⁰

Reflection-Absorption Infrared Spectroscopy (RAIRS). The RAIRS data were obtained using a Nicolet Magna-IR model 570 Series II spectrometer (Thermo Nicolet, Madison, WI) with a model FT-85 (85° grazing angle) Spectra-Tech external reflection accessory (Thermo Spectra-Tech, Shelton CT) as described elsewhere.¹⁹

RESULTS AND DISCUSSION

The SAMs of $(\text{EO})_6\text{CH}_3$ were described previously.¹⁴ For direct comparison, SAMs of $x = 6$ were prepared along with the $x < 6$ SAMs. Some of the data presented here, for $x = 6$, are new observations not in the previous report. Figures 1 and 2 show the RAIRS data between 1440 - 920 cm^{-1} and from 3120 - 2640 cm^{-1} , respectively, for the $(\text{EO})_3\text{CH}_3 - (\text{EO})_6\text{CH}_3$ SAMs. The bands at 1347, 1243, 1119, and 965 cm^{-1} (Figure 1), assigned as the symmetry designated $A_2(4)$

to A_2 (7) bands, respectively, of the 7/2 helix of the folded-chain crystal polymorph of crystalline PEO, are found in the spectra of both the $(EO)_5CH_3$ and $(EO)_6CH_3$ SAMs. The absence of additional spectral bands in this region, other than the expected OCH_3 rocking mode⁷ at 1202 cm^{-1} , indicates other OEO conformations are not present. In Figure 2, the prominent CH_2 symmetric stretch at $\sim 2894\text{ }cm^{-1}$, characteristic of a helical OEO segment^{15,20,23}, is also found in the spectra of both the $(EO)_5CH_3$ and $(EO)_6CH_3$ SAMs. Thus, within the limits of the RAIRS measurements, the TOEO segments of these SAMs are identical and essentially all in the helical conformation.

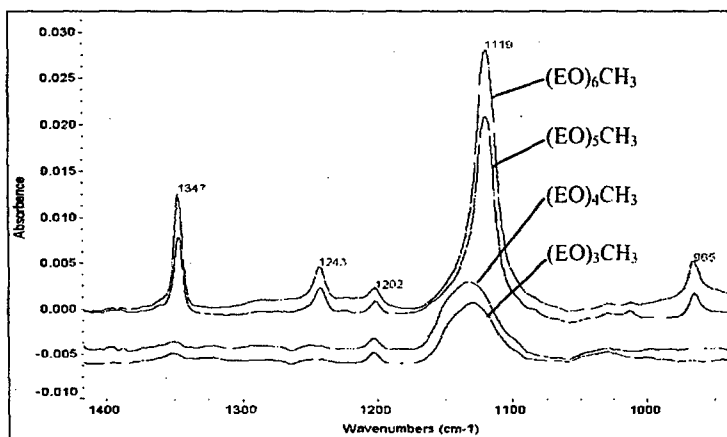


Figure 1: RAIRS spectra of $(EO)_{3-6}CH_3$ from 1420 cm^{-1} - 920 cm^{-1}

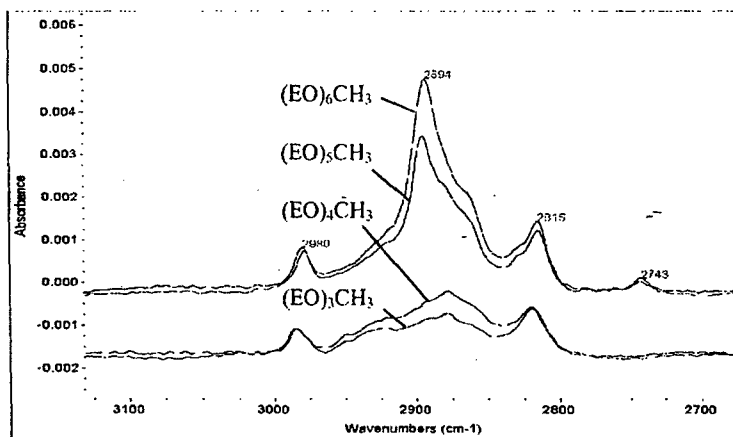


Figure 2: RAIRS spectra of $(EO)_{3-6}CH_3$ from 3120 cm^{-1} - 2680 cm^{-1}

In contrast, the RAIRS spectra of the $(EO)_3CH_3$ and $(EO)_4CH_3$ SAMs (Figures 1 and 2) are significantly different from those of $(EO)_5CH_3$ and $(EO)_6CH_3$ SAMs. The A_2 bands found in RAIRS spectra of the $(EO)_5CH_3$ and $(EO)_6CH_3$ SAMs are absent (Figure 1). The broad C-O absorption band at $\sim 1328\text{ cm}^{-1}$ is similar to that obtained for the $HS(CH_2)_{11}O(EO)_3CH_3$ SAMs⁷ and corresponds more closely to the C-O stretch of amorphous PEO.¹⁷ In Figure 2 the spectra for the $(EO)_3CH_3$ and $(EO)_4CH_3$ SAMs show a broad ensemble of bands with two maxima in the C-H stretching region at $\sim 2923\text{ cm}^{-1}$ and $\sim 2878\text{ cm}^{-1}$. These maxima more closely resemble the CH_2 asymmetric and symmetric stretch at 2930 and 2865 cm^{-1} , respectively, of molten PEO.²⁴ Thus, the RAIRS data indicate that these SAMs consist of disordered OEO segments.

The $(EO)_5CH_3$ SAMs showed variability. Figure 3 shows a comparison of the ordered, helical $(EO)_5CH_3$ SAM (top spectrum) with spectra from other samples which, in all cases, exhibited attenuation of the four A_2 bands accompanied with the appearance of a higher wavenumber shoulder on the A_2 (6) [1118 cm^{-1}] band. Similar asymmetry in the A_2 (6) band was observed for $HS(EO)_xR$ SAMs, where $x = 5$ and 7 and $R = C_{10}H_{21}$,²⁰ as well as in the $(EO)_6CH_3$ SAMs after exposure to protein¹⁴. The position of this shoulder at $\sim 1130\text{ cm}^{-1}$ is evidence of less ordered SAMs with the TOEO segments containing non-helical conformations.¹⁷

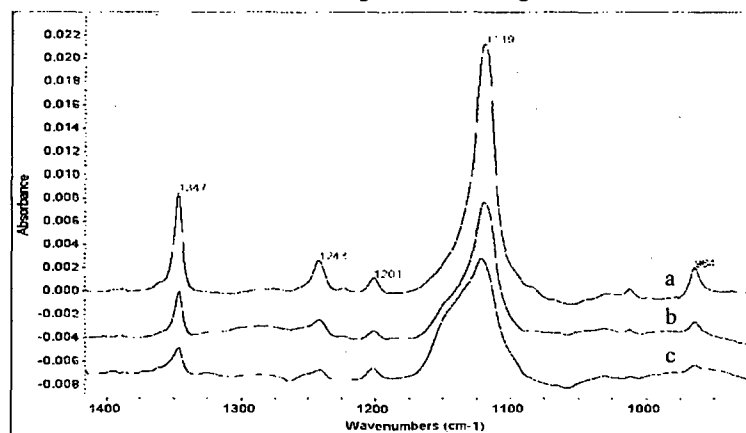


Figure 3: RAIRS spectra of three different $(EO)_5CH_3$ samples on Au. Spectrum (a) shows helical SAM. Spectra (b) and (c) show samples with small and larger amounts of non-helical OEO segments, respectively.

The cause for the variability of the $(EO)_5CH_3$ SAMs is unclear and is currently being investigated. Variability in SAMs with ω -OEO segments has been previously reported.⁷ SAM assembly parameters were varied but none afforded helical $(EO)_5CH_3$ SAMs with any increased consistency. In addition, the kinetics of formation of helical $(EO)_5CH_3$ and $(EO)_6CH_3$ SAMs were different (Table 1). Whereas SE data indicates that the $(EO)_6CH_3$ SAMs reached the expected thickness for a helical SAM after ~ 17 h, the $(EO)_5CH_3$ SAMs required significantly longer time.

Table 1. Calculated Thicknesses and SE Data for the HS(EO)₃₋₆CH₃ SAMs

Compound	Thickness, Calculated ^a (nm)			Thickness, Measured (nm ± 0.2 nm)				
	All- <i>trans</i> Extended	Helical	Disordered	17 h	28 h	2 d	6 d	8 d
HS(EO) ₃ CH ₃	1.44	1.15	< 1.15	-	0.81	0.88	0.86	0.89
HS(EO) ₄ CH ₃	1.79	1.43	< 1.43	-	1.13	1.26	1.26	1.29
HS(EO) ₅ CH ₃	2.14	1.71	< 1.71	-	1.44	1.52	1.51	1.70
HS(EO) ₆ CH ₃	2.49	1.99	< 1.99	1.97	-	1.94	-	-

^aFilm thickness calculations. (EO)₆CH₃ SAMs: helical = 1.99 nm; all-*trans* extended conformation = 2.49 nm.¹⁴ Thickness decrease/EO unit: helical = 0.28 nm²³; all-*trans* extended = 0.35 nm⁷.

CONCLUSIONS

Highly ordered (EO)₅CH₃ SAMs, with the TOEO segments in the helical conformation, are obtained and, within the limits of the RAIRS measurements, appear to be isostructural with the (EO)₆CH₃ SAMs, reported earlier.¹⁴ The highly ordered (EO)₅CH₃ SAMs take longer to form and showed variation in their molecular conformation. Many of the (EO)₅CH₃ SAMs remained less ordered, with the TOEO segments consisting of mixtures of helical and non-helical conformations. For the shorter (EO)₃CH₃ and (EO)₄CH₃ SAMs, the RAIRS spectra show bands consistent with a much more disordered, "amorphous" structure with no indication of the helical conformation. We conclude that there is no isostructural series for x = 3 - 6, due to the variability of the (EO)₅CH₃ SAMs. Also, the significant change in the TOEO conformation that occurs from x = 5 to 4 suggesting a minimum of five ethylene oxide units are necessary for a TOEO segment to adopt a helical conformation.

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21. The specification of commercial products is for clarity only and does not constitute endorsement by NIST.
22. HRMS: (EO)₆CH₃ characterized by HRMS as reported earlier.¹⁴ (EO)₅CH₃: HR FAB [M + 1]⁺ calcd for C₁₁H₂₅O₅S 269.14227; found 269.14309. (EO)₄CH₃: HR FAB [M + 1]⁺ calcd for C₉H₂₁O₄S 225.11606; found 225.11533. (EO)₃CH₃: HR FAB no mass found for C₇H₁₆O₃S; [M + 1]⁺ found for disulfide, calcd for C₁₄H₃₁O₆S₂ 359.15622; found 359.15418. 270 MHz ¹H NMR for x = 3 - 5; δ 2.70 (relative to tetramethylsilane), 2H, dt, J ≈ 6.5 Hz and 6.2 Hz; HSCH₂CH₂O)_xCH₃; 3.38, 3H, s, HSCH₂CH₂O)_xCH₃.
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